COAL AQUEOUS MIXTURES

SEYMOUR MARK

ADVANCED FUELS TECHNOLOGY
A Gulf+Western Company
Zerbe Research Center
Bethlehem, PA 18017

Coal aqueous mixtures can be prepared by simply mixing pulverized coal with water. Table 1 shows the formulation for such a slurry and compares it to one for a modern slurry.

Simple Slurry Versus Modern Slurry

A visual inspection of slurries made with these formulations would show them to be quite similar. Both would appear to be black fluids with comparable viscosities. A closer examination would reveal that the simple slurry had a considerable degree of settling while the modern slurry was uniform. Another difference between the two slurries is their concentration of coal.

Table 1 shows that the simple slurry contains 518.5 pounds of coal per hundred gallons and that the modern slurry has 725.9 pounds. Expressed another way, simple slurry contains 53% coal and modern slurry 70% coal. A comparison of the volume relationships of the ingredients in these slurries shows that simple slurry contains about 45% coal and 55% water. In the modern slurry formulation we see that the volume of coal is considerably greater than that of the water; 62.6% coal, 36.9% water. This higher ratio of coal to water is achieved in part with the use of additives. These additives, which can total only 0.5% of the weight of the slurry in some cases, not only allows a greater concentration of coal to be incorporated into the mixture; but they also disperse the particles, keep them apart and suspended in the medium, and provide the type of flow properties necessary to pump and atomize this fuel.

What are these additives, and how did they come to be used in preparing coal aqueous mixtures? The additives are primarily surface active compounds. The technology is guided by the sciences of colloid and surface chemistry, and of rheology.

Preparing Coal Aqueous Mixtures

The first challenge in preparing coal aqueous slurry is to disperse the coal particles into the medium. When coal has been ground into a powder, the coal particles can adhere to each, other in aggregates. A dispersion of the particles must be accomplished. The process involves separating the particles in an aggregate until they are dispersed. Figure 1 shows different aspects of wetting and dispersion, as now viewed. The cluster of coal particles shown as "aggregated" has various degrees of air and moisture on the surface of the particles and in the spaces between them. Work and surfactants are used to break up these aggregates, by replacing the air with water. The separated particles are shown as "wetted." They are covered with a layer of water, that has displaced the air. They also contain adsorbed surface active agents and protective colloids on their surface. Coal will occupy less space when it is wetted by a liquid, than when it is mixed with air and moisture. The volume of air displaced is considerable, it demonstrated by weighing the amount of powdered coal that can fit into a gallon container. This is generally about 4 pounds. Yet we know from our examination of a modern slurry formulation that it contains over 7.25 pounds of coal per gallon, and still has room in the container for over 3 pounds of water.

It is believed that after the coal particles are wetted-out, they disperse uniformly throughout the medium into individual pieces shown as "dispersed." The dispersed state is achieved if the particles in the suspension are separated sufficiently for the repulsive force to exceed the attractive force(1). If the attractive force is stronger, the particles are believed to re-combine as flocculates. The cluster shown as "Flocculated" differs from the aggregated cluster in that the surface of the particles and the space between them contain water rather than air. As a result they are easier to redisperse. Nevertheless, they act as if they are single large particles, and tend to settle more rapidly.

The Interaction Forces Between Particles

There are three major types of interaction forces between colloidal particles: 1. London - van der Walls, 2. Coulombic forces (DLVO), 3. Solvation, adsorbed layers(2). The effect of these forces is shown graphically in Table 2.

London - van der Waals forces are due to the influence of the dipoles within the particles acting on each other. They are attractive forces which are electromagnetic in nature. It is conventional to assign a negative value to an attraction potential and a positive value to a repulsion potential.

Coulombic forces may be either attractive or repulsive, but are almost always repulsive when dealing with coal particles dispersed in water. They are electrostatic in nature and arise from the unequal distribution of ions in solution around the particle and at its surface. This unequal distribution causes one side of the interface to acquire a net charge of a particular sign and the other side to acquire a net charge of the opposite sign, giving rise to a potential across the interface and the so-called electrical double layer[3]. The stability of a dispersion can depend upon the degree of electrostatic repulsion. The degree of which is related to the thickness of the electrical double layer.

The interplay of the electromagnetic and electrostatic forces forms the substance of the DLVO theory, which deals in a fundamental manner with the kinetics of flocculation and the stabilization of particle dispersions. Although the DLVO theory is very useful in predicting the effect of ionic surfactants as electrical barriers to flocculation, other factors must be considered to explain the effect of surfactants on dispersion stability.

Surfactants that are polymers or that have long polyoxyethylene chains may form non-electrical barriers to flocculation in aqueous media. An adsorbed layer of non-ionic surfactant on the surface of a particle can provide a steric hindrance to close particle approach by interposing a mechanical barrier. When particles collide, the distance between the surfaces is increased by twice the thickness of the adsorbed layer. When the attractive force at this distance is still sufficiently large that interaction of the adsorbed layers occurs, there is a decrease in the entropy of the system. The term "entropic repulsion" was introduced by Mackor and van der Waals in reference to the loss of movement in the tails of the adsorbed molecules when two adsorbed layers interpenetrate[4].

Properties of Coal

The water requirement of coal aqueous mixtures is a function of the properties of the constituents in the slurry. These are the coal, the water, and the additives. The chemical and physical properties of the coal have a major influence on the amount of water needed to achieve a slurry with desired flow characteristics. Coal is a heterogeneous substance that is a mixture of combustible metamorphosed plant remains that vary in physical and chemical composition[5].

Coal may be classified by rank according to fixed carbon content and heating values. Higher carbon content generally correlate with higher BTU values that designate the coals that usually make better fuels. Coals with higher volatile matter improve the combustion properties of aqueous slurries.

Coals also differ considerably in physical structure. The structure of coal can be so intricate and extensive as to make them something like a solid sponge[6].

The mineral matter and sulfur content of coal show large variations. Of course, coals that are low in these materials produce slurries that are lower in pollutants and cause less ash deposits in furnace. Another way to make slurries that are low in pollutants and less prone to furnace fouling, is to beneficiate the coal prior to its incorporation into slurry. Beneficiation processes have been developed that remove a substantial part of the ash content of a coal and lower its sulfur concentration. This can now be accomplished at very high rates of recovery and excellent slurries are being prepared with this beneficiated coal.

Coal Size Consist

Another property of coal to be studied that may influence its water requirement in aqueous mixtures is size consist. Coal with a coarse size consist has a relatively small surface area per unit weight and requires less water to coat the coal particles. Consequently, a lower amount of water is needed to fluidize the particles, and slurry of higher solids content can be produced. Coal with a fine size consist has a relatively large surface area per unit weight which requires more water to coat the coal particles. However, the finer particles may fit into the interstices between the larger particles thereby reducing the void volume.

Predictions of the packing patterns of coal particles are complicated by many factors among which are size, size distribution, and particle shape. The Rosin-Rammler relationship was developed for representing the size distribution of powdered coal(7). This formula, as well as empirical methods, have been employed to determine coal size consists that have the lowest water requirement. However, the type of particle size distribution likely to give the lowest water requirement would include sizes that might be too large for good combustion and suspension properties, and the procedures needed to produce this type of size distribution would be expensive. Certainly, economic considerations as well as fuel properties are influential in determining the size consist of coal to be used in aqueous slurry.

Slurry Formulation

Coal aqueous mixtures have been prepared containing coal, water, a nonionic surfactant, and also defoaming agents, gums and salts. Nonionic surfactants containing polyoxyethylene can be used It is believed that they lower the surface tension of the water, keep the coal particle from flocculating, promote suspension, and provide good flow properties. While playing a major role in producing coal aqueous mixtures, nonionics can be employed at concentrations of less than 0.4%.

Anti-foam agents can be used to lower the amount of foam in the slurry. Also, gums such as water soluble resins can be used to increase the viscosity of the medium. The quality of the water can also influence the stability of the slurry and its solid concentration. Water can contain soluble minerals which become electrolytes in the slurry, that can have an effect on the electrical balance of the system. Slurries stabilized with non-ionic surfactants are less susceptible to their influence.

NonIonic Surfactants

Some nonionic surfactants that contain long chains of polyoxyethylene are shown in Figure 2. Figure 2a shows a surfactant having an ethylene diamine backbone, which is a block polymer containing chains of propylene oxide and ethylene oxide of various lengths. Another compound of this type containing chains of propylene oxide and ethylene oxide is shown in Figure 2b. This surfactant has a propylene glycol base. The formula shown in Figure 2c contains a single chain of ethylene oxide attached to a nonylphenoxy group. It has no propylene oxide.

Each of the formulas shown in Figure 2 represent a different series. The individual surfactants in each series differ from each other primarily by the length of the ethylene oxide chain. The moles of ethylene oxide on these molecules range from 4 to over 300.

The nonionic compounds are polar and have hydrophobic and hydrophillic portions. In coal aqueous mixtures, the hydrophobic end of the surfactant is believed oriented toward the coal particle and the hydrophillic end toward the aqueous medium. In Figure 2a, the hydrophobic portion encompasses the ethylene diamine and propylene oxide part of the molecule. For the molecule shown in Figure 2b, it is the propylene glycol portion together with the propylene oxide chain that comprises the hydrophobic segment of the surfactant, and in Figure 2c, the nonyl hydrocarbon chain and benzene ring are the hydrophobic end of the compound. For all these molecules, it is the ethylene oxide portion that is hydrophillic. For each of the compounds, those with the highest molecular weight in the series have the longest polyoxyethylene chains. The longer the chain of ethylene oxide, the further they extend into the solution.

Experiments

Experimental work done with these surfactants in coal aqueous slurry was revealing. A comparison of the compounds that were effective in producing a 70% solids slurry, with those that were not, showed that between the primary difference between them was in the ethylene oxide content. The surfactants that were found effective contained 100 or more moles of ethylene oxide, while all that were not, contained less. Molecular weight did not appear to be as influential because two of the compounds deemed not effective had higher molecular weights than the one that was.

Slurry Properties

Coal aqueous mixtures are designed to conform to two major catagories of properties: fuel and rheological. Fuel properties relate to the BTU content of the slurry, its level of ash, sulfur, and volatile matter, and sieve analysis. Rheological properties are concerned with the flow and handling characteristics of the slurry, and its stability to settling and shear.

A viscosity profile of a coal aqueous slurry is shown in Figure 3. This slurry exhibits desired rheological properties; its viscosity is well above 10,000 centipoise at low shear rates of 0.3 sec^{-1} and below, and it is lower than 2000 cP at shear rates above 100 sec^{-1}. The high viscosity at low shear rates indicates that this slurry will resist settling when it is at rest. The lower viscosity at 100 sec^{-1} indicates that it will pump readily. Shear rates during atomization are estimated to be at least 10,000 sec^{-1}. The curve in Figure 3 suggests that the viscosity of this slurry at that shear rate will be low, and that it will atomize well.

Slurries that decrease in viscosity with increased shear stress are described as pseudoplastic, and the curve in Figure 3 shows a material with this property. If this slurry was measured at even lower shear rates, and the data showed that flow did not begin until a certain minimum shear stress was exceeded, then the slurry could be described as a Bingham plastic. The point at which flow starts in such a system is called yield value, which is often manifested in materials with high concentrations of powder dispersed in liquids.

Summary

Coal aqueous mixtures can be prepared that have high coal content, are stable to settling, and can be pumped and atomized. The concentration of coal in a slurry depends upon the water requirement of the system. This requirement is effected by the grade of coal used, its size consist, and upon the additives in the formulation. Of particular importance is the type of surfactant used. Surfactants lower the surface tension of water and adsorb at the solid/solution interface to hinder close particle approach, ionic surfactants do so primarily by electrostatic repulsion. Nonionic surfactants do so primarily by steric hindrance.

Coal aqueous slurry can be made at a cost that is lower than that of No. 6 fuel oil by over $1.00 per million BTU. This differential has provided the economic incentive to develop aqueous slurry as a replacement fuel. The findings presented in this study, and in work done by others in the industry, indicate that the research in this field has succeeded in developing a new fuel.

REFERENCES

1. Parfitt, G. D., Dispersion of Powders in Liquids, Elsevier, Amsterdam, 1969.

2. Patton, T. C., Paint Flow and Pigment Dispersion, Wiley, New York, 1979.

3. Rosen, M. J., Surfactants and Interfacial Phenomena, Wiley, New York, 1979.

4. Matijevic, E., Surface and Colloid Science, Volume 8, Wiley, New York, 1976.

5. Leonard, J. W., Mitchell, D. R., Coal Preparation, The American Institute of Mining, Metallurgical, and Petroleum Engineers Inc., New York, 1966.

6. Berkowitz, N., An Introduction to Coal Technology, Academic Press, New York, 1979.

7. Cadle, R. D., Particle Size, Reinhold Publishing Corp., New York, 1965.

Figure 1

ASPECTS OF WETTING AND DISPERSION

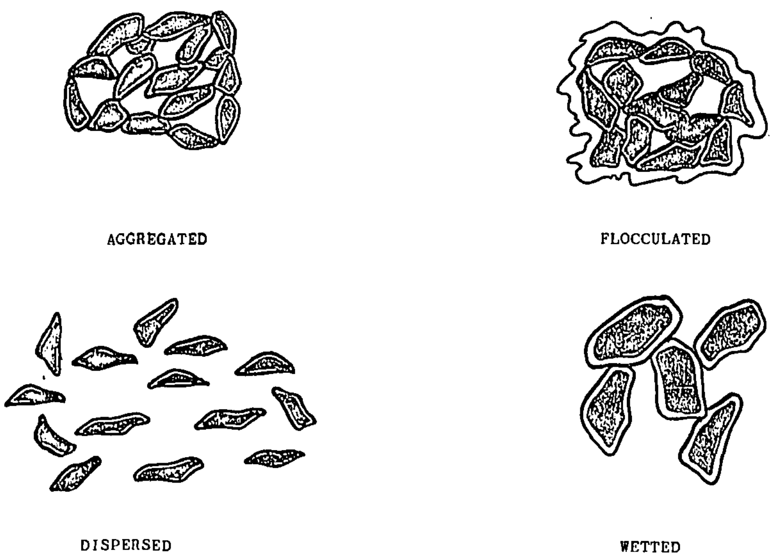
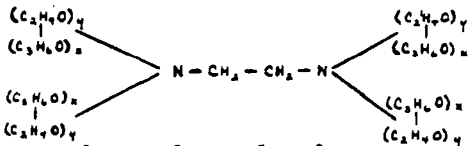
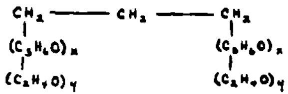


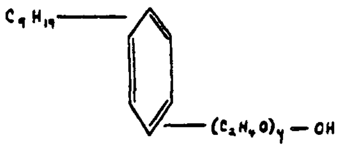
FIGURE 2 NONIONIC SURFACTANTS



A. PROPOXYLATED, ETHOXYLATED, ETHYLENE DIAMINE



B. PROPOXYLATED, ETHOXYLATED, PROPYLENE GLYCOL



C. NONYLPHENOXY POLYETHYLENEOXYETHANOL

Figure 3

VISCOSITY PROFILE

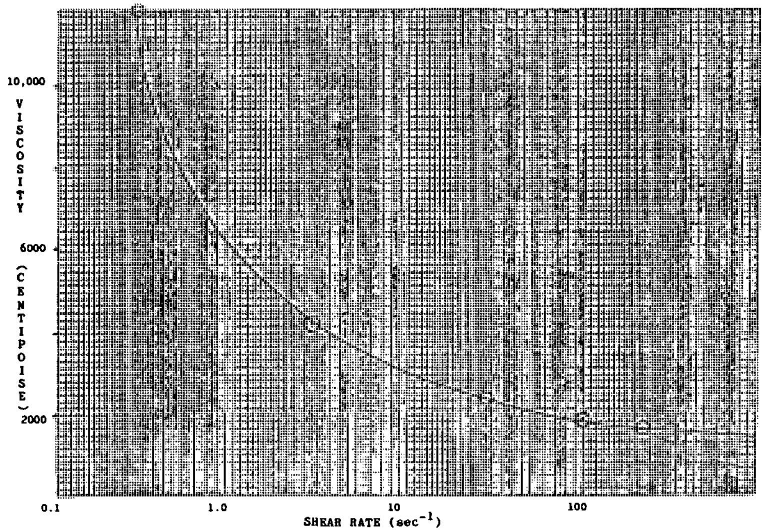


Table 1

Coal Aqueous Mixture Formulations

(per 100 gallons slurry)

	Simple Slurry			Modern Slurry		
	Weight		Volume	Weight		Volume
	Lb.	%	(Gal.)	Lb.	%	(Gal.)
Coal (MF)	518.5	(53.0)	44.7	725.9	(70.0)	62.6
Water	460.1	(47.0)	55.3	306.6	(29.5)	36.9
Additives				5.0	(0.5)	0.5
	978.6		100.0	1037.5		100.0

Table 2

Interaction Forces Between Particles

		Forces	+ -	Nature
DLVO THEORY	1.	London	Attraction	Electromagnetic
	2.	Coulombic	Primarily Repulsion	Electrostatic (Electrical Double Layer)
STERIC HINDRANCE THEORY	3.	Solvation	Repulsion	Adsorbed Layers Entropic